

THEORETICAL INVESTIGATION OF PROTONATED CARBON DIOXIDE

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The equilibrium structure of CO_2H^+ has been obtained from self-consistent field and configuration interaction wavefunctions. Only one stable form has been found, a linear $\text{O}-\text{C}-\text{O}$ chain with the hydrogen bonded to oxygen and slightly off axis, in analogy with known isoelectronic species. A second structure protonated at carbon, which has been inferred from mass spectrometric studies, is found to be unstable with respect to spontaneous rearrangement. The proton affinity of CO_2 is calculated to be 136 kcal/mole, in reasonable agreement with the most recent experimental value.

1. Introduction

The protonation reaction



is of special interest because of its pivotal role in aqueous acid–base chemistry. The (gas phase) energy released in reaction (1) is defined as the proton affinity (PA) of species A. Protonated species have recently aroused further interest due to their apparent role in the formation of complex molecules in interstellar space [1]. It is thought that cosmic rays act on the dominant molecular component of the interstellar gas, H_2 , to form H_3^+ ions, and these form protonated species via



Other mechanisms which form protonated species are hydrogen atom abstraction



and proton transfer,



The energetics and kinetics of these reactions have been extensively studied in the laboratory; see, e.g., Ausloos [2] and Ferguson [3]. The structure and bonding of protonated species, on the other hand, have generally not been determined. This is due to the difficulty of obtaining spectral data – especially microwave rotational spectra which are traditionally the most reliable clues to molecular structure – for ionic species. In fact, the first identification of a microwave transition in a molecular ion came from astronomical and not laboratory observations.

Buhl and Snyder [4] observed a line at 89.190 GHz in the direction of the Orion nebula which could not be identified with any known terrestrial species. Based

on the expectation that it would be abundant in the interstellar medium and an intuitive estimate of its structure, Klemperer [5] suggested that this line arose from HCO^+ ; large-scale quantum calculations for the rotational frequency of HCO^+ [6] supported this assignment. Subsequently, Turner [7] observed a triplet of lines near 93.174 GHz and, again based largely on quantum mechanical calculations, N_2H^+ was suggested as the carrier of these lines [8]. Spurred on by these astrophysical observations, renewed attempts to observe microwave spectra of molecular ions in the laboratory have very recently been successful, confirming both of these identifications [9].

The discovery of interstellar protonated N_2 suggests an interesting point [10]. Many species which may be abundant in interstellar space are not amenable to radiofrequency observation because they are too symmetric to possess a permanent electric dipole moment and so do not display a pure rotational spectrum. Protonation will, in most cases, sufficiently lower the symmetry, rendering such species "visible". Thus, according to current theories of interstellar chemistry, the presence of N_2H^+ implies that N_2 is rather abundant. A number of other cases come to mind where observations of the protonated species might be the best way of inferring the existence of an interstellar molecule. The obstacle to this approach, of course, is lack of information about rotational frequencies of the molecular ions.

Since quantum calculations were so useful in the identification of interstellar HCO^+ and N_2H^+ , one might hope that similar calculations could be used to *predict* frequencies for other species which could then be used as the basis for an astrophysical (or laboratory) search. A difficulty is the inherent limit of accuracy in current ab initio techniques: uncertainties in predicted frequencies would necessitate searches that are only marginally feasible with current equipment. Nevertheless, the prospect of identifying other interstellar molecules, coupled with the general interest in energetics and structure of protonated species, seemed adequate to justify large-scale ab initio calculations for selected ions and was the motivation for the study of protonated CO_2 reported here.

Several workers have studied protonated CO_2 by mass spectrometrically monitoring its appearance potential from various organic precursors. These data are generally converted to a standard heat of formation,

$$\Delta H_f(\text{CO}_2\text{H}^+), \text{ which is related to the proton affinity as } \text{PA}(\text{CO}_2) = -[\Delta H_f(\text{CO}_2\text{H}^+) - \Delta H_f(\text{H}^+) - \Delta H_f(\text{CO}_2)]. \quad (5)$$

(The difference between values at room temperature and absolute zero, about 2 kcal/mole, will be neglected here since this is smaller than either experimental or theoretical uncertainties.) The heats of formation of H^+ and CO_2 are well known:

$$\Delta H_f(\text{H}^+) = 15.85 \text{ eV} = 366 \text{ kcal/mole}, \quad (6)$$

$$\Delta H_f(\text{CO}_2) = -4.07 \text{ eV} = -94 \text{ kcal/mole}. \quad (7)$$

Bernecker and Long [11] obtained $\Delta H_f(\text{DCO}_2^+) = 166 \text{ kcal/mole}$ from $\text{DCO}_2\text{C}_2\text{H}_5$, and $\Delta H_f(\text{CO}_2\text{H}^+) = 161 \text{ kcal/mole}$ from $\text{C}_2\text{H}_5\text{CO}_2\text{H}$. As indicated by the two notations, these authors assumed that this data referred to two geometrical structures, HCO_2^+ with the proton bonded to carbon (cf. fig. 1) and CO_2H^+ with the proton bonded to oxygen (cf. fig. 2), which would result if there were no rearrangement from the parent species. Pritchard, Thynne, and Harrison [12], using DCO_2H as a precursor, also assumed no rearrangement and obtained values $\Delta H_f(\text{DCO}_2^+) \leq 143 \text{ kcal/mole}$ and

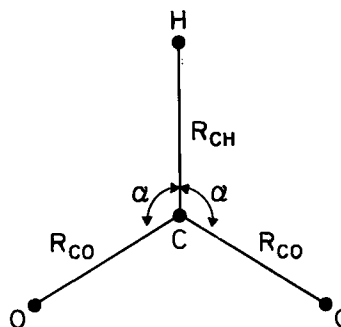


Fig. 1. Coordinates used to describe Structure I.

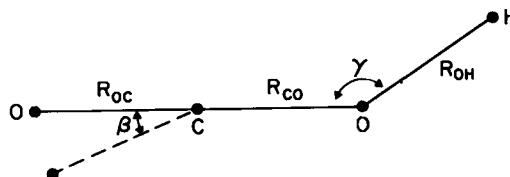


Fig. 2. Coordinates used to describe Structure II ($\beta = 0$) and non-linearity of the O-C-O chain ($\beta \neq 0$).

$\Delta H_f(\text{CO}_2\text{H}^+) = 152$ kcal/mole. Using $\text{CH}_3\text{CO}_2\text{H}$ as a precursor, Haney and Franklin [13] obtained $\Delta H_f(\text{CO}_2\text{H}^+) = 145$ kcal/mole where "the expected structure of this ion would be COOH^+ instead of HCO_2^+ unless a rearrangement occurs". These measurements lead to $\text{PA}(\text{CO}_2) = 117 \pm 11$ kcal/mole with more recent measurements favoring higher values. Thus $\text{PA}(\text{CO}_2)$ is somewhat smaller than that for carbon monoxide, $\text{PA}(\text{CO}) = 137$ kcal/mole, a value whose determination from similar experiments has a history of comparably large uncertainties.

Although there is no experimental information concerning the structure of CO_2H^+ , this ion is isoelectronic with HN_3 (hydrazoic acid), HNCO (isocyanic acid), HOCN (cyanic acid), and HCNO (fulminic acid), and is therefore expected to have a similar structure. Microwave spectra for HN_3 , HNCO , and HCNO have been interpreted in terms of a linear chain of the three heavy atoms with the hydrogen slightly off axis. A number of related halo- and methyl-substituted species as well as the thio-analogs also appear to have this structure. However, the possibility of large amplitude bending vibrations and non-linearity of the three heavy atoms have also been suggested for several of these species.

The calculations reported here were meant to answer several questions: (1) What is the equilibrium structure of CO_2H^+ ? This can be used to predict the microwave rotational spectrum. (2) Is there another, metastable structure as inferred from the mass spectrometric studies? (3) What is the proton affinity of CO_2 ? The relative proton affinities of CO and CO_2 may have implications for interstellar chemistry.

2. Details of calculation

The potential energy surface for a molecule with four atoms depends on six internal coordinates. Because a complete survey of the six-dimensional surface would require an unreasonable effort, computations have been limited, for the most part, to two likely configurations. Structure I (cf. fig. 1) corresponds to protonation at carbon. Overall C_{2v} symmetry has been imposed; i.e., the proton approaches along the bisector of the $\text{O}-\text{C}-\text{O}$ angle, and the surface is a function of only three parameters, the $\text{C}-\text{H}$ distance, the two (equal) $\text{O}-\text{C}$ distances, and α the

Table 1

Contraction coefficients and orbital exponents (in parentheses) for gaussian atomic orbital basis set. Polarization functions used in the larger calculation are indicated by (P)

Carbon	1s	.002029(4232.61)+.015535(634.882) +.075411(146.097)+.257121(42.4974) +.596555(14.1892)+.242517(1.9666)
	1s'	1.0(5.1477)
	2s	1.0(0.4962)
	2s'	1.0(0.1533)
	2p	.018534(18.1557)+.115442(3.9864) +.386206(1.1429)+.640089(0.3594)
	2p'	1.0(0.1146)
	(P) 3d	1.0(1.0)
Oxygen	1s	.002031(7816.54)+.015436(1175.82) +.073770(273.188)+.247606(81.1696) +.611832(27.1836)+.241205(3.4136)
	1s'	1.0(9.5322)
	2s	1.0(0.9398)
	2s'	1.0(0.2846)
	2p	.019580(35.1832)+.124189(7.904) +.394727(2.3051)+.627375(0.7171)
	2p'	1.0(0.2137)
	(P) 3d	1.0(1.0)
Hydrogen	1s	.019671(13.0171)+.137917(1.963) +.478287(0.444647)
	1s'	1.0(0.121964)
	(P) 2p	1.0(1.0)

$\text{O}-\text{C}-\text{O}$ angle. Structure II (cf. fig. 2) corresponds to protonation at oxygen, the structure expected by analogy with isoelectronic species. The $\text{O}-\text{C}-\text{O}$ chain has been constrained to be linear here so the surface depends on four dimensions, the $\text{O}-\text{C}$ distance, the $\text{C}-\text{O}$ distance, the $\text{O}-\text{H}$ distance, and γ the $\text{C}-\text{O}-\text{H}$ angle. Even with these restrictions a large number of points must be sampled so that a fairly cheap level of ab initio approximation was desired. For this, self-consistent field (SCF) calculations using a double-zeta (DZ) basis were employed. The DZ basis includes two

contracted gaussian functions [14] for each nl shell in the separated atoms (cf. table 1). Although DZ SCF calculations are relatively cheap, requiring 1–2 min (all times quoted are for an IBM 360/95) of computer time per geometry, they generally give semi-quantitative predictions of molecular structure. To obtain the final equilibrium geometry, more accurate calculations were done for Structure II. Augmenting the basis set with polarization functions (cf. table 1) SCF calculations were performed, followed by configuration interaction (CI) [15] including all single and double excitations from the SCF orbitals (except for the 1s core orbitals on carbon and oxygen). This is nearly the same level of accuracy used in recent calculations for HCO^+ [6], and HCN and HNC [16], in which computed bond lengths were found to agree with experiment to better than 0.005 Å.

Some of the DZ SCF results for Structure I are summarized in table 2. The C–O distance was fixed initially at $R(\text{C–O}) = 1.162$ Å, the experimental distance in CO_2 . As the proton approaches carbon along the perpendicular, the interaction is initially repulsive; there is a shallow local minimum near $R(\text{C–H}) = 1.4$ Å but this is above the asymptotic limit. The effect of

stretching the C–O distance and bending the O–C–O angle were also considered near this local minimum. As seen in table 2, the energy is *slightly* lowered by stretching the bonds and bending the oxygens toward the proton by a few degrees, but the lowest energy found is still above the asymptotic limit.

The long-range repulsive interaction found here may seem unusual in relation to the often discussed charge-induced-dipole which, for ion–molecule interactions, always leads to a long-range R^{-4} attraction. However, the angle-dependent charge-quadrupole interaction is of even longer range, varying as R^{-3} , and it is repulsive for this angle of approach.

A number of DZ SCF calculations were also done for Structure II. These will not be presented since the SCF CI values discussed below are more accurate. Suffice it to note here that DZ SCF predicted an equilibrium geometry with $R(\text{O–C}) = 1.124$ Å, $R(\text{C–O}) = 1.224$ Å, $R(\text{O–H}) = 0.978$ Å, and $\gamma = 129^\circ$ with an energy of -187.7590 hartree which is more than 5 eV below any energy found for Structure I. The DZ SCF bond distances are in excellent agreement with the more accurate SCF CI values, but the predicted bond angles differ by about 11° .

These calculations seemed to imply that protonated CO_2 possessed only one stable configuration, corresponding to Structure II. A few additional calculations were performed to see if there might be a barrier to rearrangement starting from near the local minimum found for Structure I. With the two C–O distances fixed at 1.162 Å and the C–H distance fixed at 1.389 Å, the proton was moved from the perpendicular ($\theta = 90^\circ$, cf. fig. 3) to $\theta = 45^\circ$. This produced a continuous lowering of the energy as summarized in table 3. No attempt was made to find a minimum energy path, but it is apparent that *Structure I is not stable with respect to spontaneous rearrangement to Structure II*.

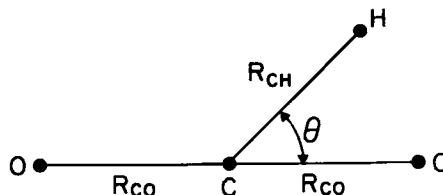


Fig. 3. Coordinates used in calculations to search for a barrier to rearrangement.

Table 2

Energy of CO_2 protonated at carbon (cf. fig. 1) from DZ SCF calculations. Bond lengths are in angstroms; α , the HCO bond angle is in degrees; and the energy is in hartree atomic units

$R(\text{CH})$	$R(\text{CO})$	α	Energy
∞	1.162	90	-187.5533
5.821	1.162	90	-187.5515
4.234	1.162	90	-187.5489
2.117	1.162	90	-187.5388
1.852	1.162	90	-187.5412
1.455	1.162	90	-187.5475
1.389	1.162	90	-187.5475
1.323	1.162	90	-187.5464
1.191	1.162	90	-187.5382
1.389	1.162	92	-187.5460
1.389	1.172	90	-187.5487
1.389	1.183	90	-187.5490
1.389	1.193	90	-187.5484
1.389	1.183	88	-187.5498
1.389	1.183	86	-187.5502
1.389	1.183	84	-187.5500
1.421	1.183	86	-187.5505
1.450	1.183	86	-187.5506
1.468	1.183	86	-187.5505

Table 3

Energy of CO_2H^+ from DZ SCF calculations for selected points along the path interconnecting Structure I (protonation at carbon) and Structure II (protonation at oxygen). The C–O bond lengths have been fixed at 1.162 Å and the C–H bond length at 1.389 Å. The HCO angle, θ , is varied as indicated in fig. 3. The energy is in hartree atomic units

θ (deg)	Energy
90	–187.5475
88	–187.5480
85	–187.5506
60	–187.6215
45	–187.6691

Table 4

Energy (in hartree atomic units) of CO_2 as a function of the C–O bond length (Å) from SCF and CI calculations using the double zeta plus polarization basis listed in table 1

R(CO)	E(SCF)	E(corr.)	E(total)
1.111	–187.67029	–0.41586	–188.08615
1.154	–187.67440	–0.42317	–188.09757
1.159	–187.67364	–0.42408	–188.09772
1.164	–187.67264	–0.42498	–188.09762
1.169	–187.67140	–0.42589	–188.09729
1.217	–187.65088	–0.43390	–188.08478

Starting from SCF calculations with the full (DZ plus polarization) basis set in table 1, CI calculations were done using the MOLECULE-CI program [15]. To gauge reliability of the methods, calculations were done first on CO_2 . These calculations are fairly cheap; taking advantage of the three planes of symmetry, computer time – including integral evaluation, SCF, integral transformation, and CI with 48 single and 5152 double excitations – was about 15 min. Results are given in table 4. The predicted C–O equilibrium distance of 1.159 Å can be compared with the experimental value of 1.162 Å [17].

A number of calculations were then done for CO_2H^+ to find the minimum energy within the constraints of Structure II. Due mostly to the lowering of symmetry to only one reflection plane the number of configurations increases to 190 single and 25648 double excitations; the computer time is increased accordingly to about 55 min per geometry. Results of these calculations are presented in table 5. The mini-

Table 5

SCF and CI energy of CO_2H^+ as a function of geometry for Structure II (cf. fig. 2). The O–C–O group has been constrained to be linear ($\beta = 0$). The double zeta plus polarization basis set is listed in table 1. Values with an asterisk have been interpolated from the preceding values. Distances are in angstroms, the angle γ is in degrees, and energies are in hartree atomic units

R(OC)	R(CO)	R(OH)	γ (COH)	E(SCF)	E(corr.)	E(total)
1.159	1.159	23.66	116.57	–187.67359	–0.42416	–188.09775
1.159	1.159	0.963	115.0	–187.874228	–0.428362	–188.302590
1.159	1.159	0.963	120.0	–187.875493	–0.428197	–188.303690
1.159	1.159	0.963	125.0	–187.875838	–0.428070	–188.303908
1.159	1.159	0.963	130.0	–187.875441	–0.427967	–188.303408
1.159	1.159	0.963	123.87*	–188.303929*
1.159	1.159	0.979	123.87	–187.876072	–0.428309	–188.304381
1.159	1.159	0.995	123.87	–187.875864	–0.428516	–188.304380
1.159	1.159	0.987*	123.87	–188.304437*
1.159	1.159	0.987	126.0	–187.875983	–0.428362	–188.304345
1.159	1.159	0.987	122.0	–187.875940	–0.428462	–188.304402
1.159	1.159	0.987	123.52*	–188.304436*
1.159	1.175	0.987	123.52	–187.877902	–0.429297	–188.307199
1.159	1.196	0.987	123.52	–187.878904	–0.430416	–188.309320
1.159	1.228	0.987	123.52	–187.877636	–0.431992	–188.309628
1.159	1.249	0.987	123.52	–187.875247	–0.432977	–188.308224
1.159	1.215*	0.987	123.52	–188.309881*
1.181	1.215	0.987	123.52	–187.871717	–0.433761	–188.309478
1.138	1.215	0.987	123.52	–187.883653	–0.428872	–188.312525
1.101	1.215	0.987	123.52	–187.887605	–0.424405	–188.312010
1.059	1.215	0.987	123.52	–187.882123	–0.419138	–188.301261
1.122*	1.215	0.987	123.52	–188.313176*
1.122	1.215	0.987	126.0	–187.885747	–0.426862	–188.312609
1.122	1.215	0.987	121.0	–187.886586	–0.426975	–188.313561
1.122	1.215	0.987	117.0	–187.886613	–0.427102	–188.313715
1.122	1.215	0.987	113.0	–187.885963	–0.427270	–188.313233
1.122	1.215	0.987	117.95*	–188.313733*
1.122	1.215	0.963	117.95	–187.886541	–0.426701	–188.313242
1.122	1.215	1.005	117.95	–187.886082	–0.427344	–188.313426
1.122	1.215	0.987*	117.95	–188.313733*
1.122	1.231	0.987	117.95	–187.885998	–0.427780	–188.313778
1.122	1.247	0.987	117.95	–187.884663	–0.428461	–188.313124
1.122	1.210	0.987	117.95	–187.886722	–0.426825	–188.313547
1.122	1.224*	0.987	117.95	–188.313844*
1.138	1.224	0.987	117.95	–187.883790	–0.429387	–188.313177
1.106	1.224	0.987	117.95	–187.887686	–0.425536	–188.313222
1.121*	1.224	0.987	117.95	–188.313844*
1.121	1.224	0.987	120.0	–187.886368	–0.427345	–188.313713
1.121	1.224	0.987	116.0	–187.886346	–0.427482	–188.313828
1.121	1.224	0.987	117.20*	–187.886422	–0.427437	–188.313859

imum energy is found at $R(\text{O}-\text{C}) = 1.121 \text{ \AA}$, $R(\text{C}-\text{O}) = 1.224 \text{ \AA}$, $R(\text{O}-\text{H}) = 0.987 \text{ \AA}$, and $\gamma = 117.2^\circ$. These bond distances are in excellent agreement with the DZ SCF predictions, but the hydrogen is predicted to be much further off axis.

From the predicted geometry, CO_2H^+ is a near-symmetric top. The rotation constants for the normal isotopic species are $C = 10.66 \text{ GHz}$, $B = 10.82 \text{ GHz}$, and $A = 706.0 \text{ GHz}$. Based on these predicted frequencies, a preliminary search for interstellar CO_2H^+ was made in November 1974 with negative results [10].

The permanent dipole moment of CO_2H^+ has been computed from the SCF function at the calculated equilibrium geometry. Measured from the center of mass for the normal isotopic species, the component of the dipole moment parallel to $\text{O}-\text{C}-\text{O}$ is 2.0 D and the perpendicular component is 2.8 D. In both cases, the positive end is toward the proton. These values are estimated to be accurate to $\pm 0.5 \text{ D}$ [18].

The proton affinity of CO_2 is predicted by the SCF CI calculation to be $5.88 \text{ eV} = 136 \text{ kcal/mole}$. (The DZ SCF value is about 10% lower than this, but the SCF value with the larger basis is within 2% of the CI value.) By comparison, the SCF value for CO is 142 kcal/mole [19]. This is consistent with the experimental measurements of $\text{PA}(\text{CO}_2) = 117 \text{ kcal/mole}$ and $\text{PA}(\text{CO}) = 136 \text{ kcal/mole}$, where the experimental uncertainties are $\pm 10 \text{ kcal/mole}$. The theoretical values are estimated to have comparable uncertainties and are also a few kcal/mole too large due to zero-point vibration. From consideration of the experimental and theoretical results, it appears that the proton affinity of CO is larger than that of CO_2 by only 5–10 kcal/mole. This implies that $\text{PA}(\text{CO}_2)$ is near the upper end of the experimental range of values, in accord with the more recent measurements.

Finally, the possibility of an equilibrium structure with a non-linear $\text{O}-\text{C}-\text{O}$ chain must be considered. Recently, Harrison et al. [20] have predicted a non-linear N_3 group in hydrazoic acid from a limited number of large basis set SCF calculations. These authors cite an analysis of infra-red bending spectra [21] as implying a non-linear structure in HN_3 , but this seems to be a misinterpretation since the model used in that study assumed a *linear equilibrium configuration* of the N_3 group. As discussed by Pauling [22], reasonable valence bond structures for the isoelectronic species HN_3 and HNCO all predict the three heavy

atoms to be linear. Spectra of HN_3 , HNCO , and also HCNO have been interpreted in terms of a linear backbone, although anomalies due to large amplitude bending of the *hydrogen* have been noted. (See, e.g., Winnewisser et al. [23] and references therein; also Stone [24].) A related species for which a *bent* (planar) structure is known is chlorine isocyanate, ClNCO [25]. The slight departure ($< 10^\circ$) from linearity found here for the $\text{N}-\text{C}-\text{O}$ group can be understood in terms of a small contribution from a valence bond structure with a $\text{Cl}-\text{N}$ double bond. But, since hydrogen does not form double bonds, such a structure should not contribute to the protonated species.

The expectation of a linear $\text{O}-\text{C}-\text{O}$ chain notwithstanding, some exploratory DZ SCF calculations were done to consider this point, although an exhaustive optimization of all degrees of freedom seemed prohibitive. To consider possible non-planar structures, calculations were done with one of the carbon or oxygen atoms raised above the plane; in each case the energy increased. On the other hand, the energy was slightly, but significantly lowered for planar structures with the end oxygen bent away from the proton. Keeping the bond lengths and $\text{O}-\text{C}-\text{H}$ angle fixed at the values listed above for the DZ SCF minimum for Structure II, an energy minimum was found near $\beta = 5^\circ$ (cf. fig. 2) with an energy about 100 cm^{-1} lower than the linear, $\beta = 0^\circ$, value. This is entirely analogous to the behavior found for NH_3 by Harrison et al. [20]. Based on the discussion above, it is believed that CO_2H^+ and its isoelectronic analogues have a linear backbone and that the non-linearity found here and in ref. [20] is an artifact of the level of *ab initio* approximation. Although expensive, it would however be most desirable to do further calculations including correlation to map out the potential surface near the minimum and to consider a proper vibrational average over this surface to compare with available experimental data.

3. Summary

The equilibrium geometry of CO_2H^+ has been obtained by large-scale *ab initio* calculations. Only one stable configuration was found, with the proton bonded to oxygen, somewhat off axis from a linear

O—C—O chain. This is analogous to the isoelectronic species, hydrazoic acid, isocyanic acid, and fulminic acid. An alternate structure, protonated at carbon, which has been inferred from mass spectrometric appearance potentials, was shown to be unstable with respect to spontaneous rearrangement; these data must be reinterpreted in terms of differing "excitation energies" associated with the rearrangement.

The proton affinity of CO₂ was calculated to be 136 kcal/mole which is in reasonable agreement with the most recent experimental value [13] of 127 kcal/mole, especially recalling that the theoretical value is a few kcal/mole too high due to neglect of zero-point motion. The proton affinity of CO₂ is thus 5–10 kcal/mole lower than that of carbon monoxide.

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